LEACHING MODELS FOR SUBSURFACE POLLUTION ASSESSMENT IN AGROECOSYSTEMS

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Abstract

Unrestricted use of pesticides in agriculture threatens ground-water resources and can have adverse ecological impact on the nation's receiving surface waters. In this paper, we develop mass fraction models for exposure assessment and the regulation of agricultural organic chemicals. The models are obtained by applying the method of Laplace transformation to solute fate and transport equations. The models describe residual mass emissions of pesticides below the root zone, to the water table, and in aquifers. They emphasize the physical and biochemical processes responsible for the fate and transport of organic solutes in the subsurface and their relationship to chemical properties and a set of environmental factors. The potential of the use of the mass fraction models in the management of agriculture pesticides is also investigated. A combined modeling and ArcView GIS framework is used to assess soil and groundwater vulnerability to the pesticide dicamba (commonly used for soybean and grains) in an agricultural watershed in the Mid-Atlantic Coastal plain.

Introduction

Pesticides used in crop production are a major source of nonpoint source pollutants to ground water, and their discharge to the nation's surface water may be a contributing factor toward the decline of the living resources and the deterioration of ecosystems. Cost-effective assessment tools are needed to regulate the use of agricultural chemicals, identify areas which are potentially vulnerable to nonpoint-source pollution, and support ecosystem restoration goals by improving the nation's water quality. Physically based environmental simulation models can be cost-effective tools for resource managers when compared to costly and prolonged field monitoring strategies. In this effort, we model solute leaching in two distinct soil compartments, the soil-root layer and intermediate-vadose zone, and implement them within ArcView GIS to agricultural watersheds in the Mid-Atlantic coastal plain.

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Leaching models or indices are used for screening organic chemicals relative to their mobility in the soil (*Laskowski et al.*, 1982; *Jury et al.*; 1984*Rao et al.*, 1985; *Mahmood and Sims*, 1986; and *Meeks and Dean*, 1990). *Beltman et al.* (1995) developed mass fraction models that describe leaching in the soil and subsequent mixing and attenuation in ground water. Although index models are not suitable for predicting concentrations, they nevertheless are simple and require data that are generally available from scientific literature and soil survey reports. Further, they can be integrated with GIS and produce an effective assessment tool for the management of nonpoint source in agricultural watersheds (e.g., *Khan and Liang*, 1989, and *Loague et al.* 1995).

Leaching Below the Root Zone

Fig. 1 illustrates the conceptual soil ground-water system that is modeled here. We assume soluble fraction of pesticide mass per unit area of soil, M_o [Kg], is instantaneously mobilized at the surface by infiltrating water into the root zone. This may be represented mathematically by a Dirac-delta pulse of input mass for which the average solute concentration in the root zone is governed by the following equation (*Hantush and Mariño*, 1997), written in the differential form

$$dC_r + \beta_r C_r \, dt = \frac{M_0}{\theta_r h R_r} \delta(t) \, dt \tag{1}$$

where $\beta_r = \left[1 + \ln(2)(T_r/\lambda)(1+\mu)\right]/T_r$; $C_r(t)$ = average concentration in the root zone [Kg/m^3]; $T_r = h R_r/(v^*/\theta_r)$ is the residence time in the root zone [day]; v^* = percolation below the root zone [m/day] - equals to precipitation plus irrigation rate minus evapotranspiration,
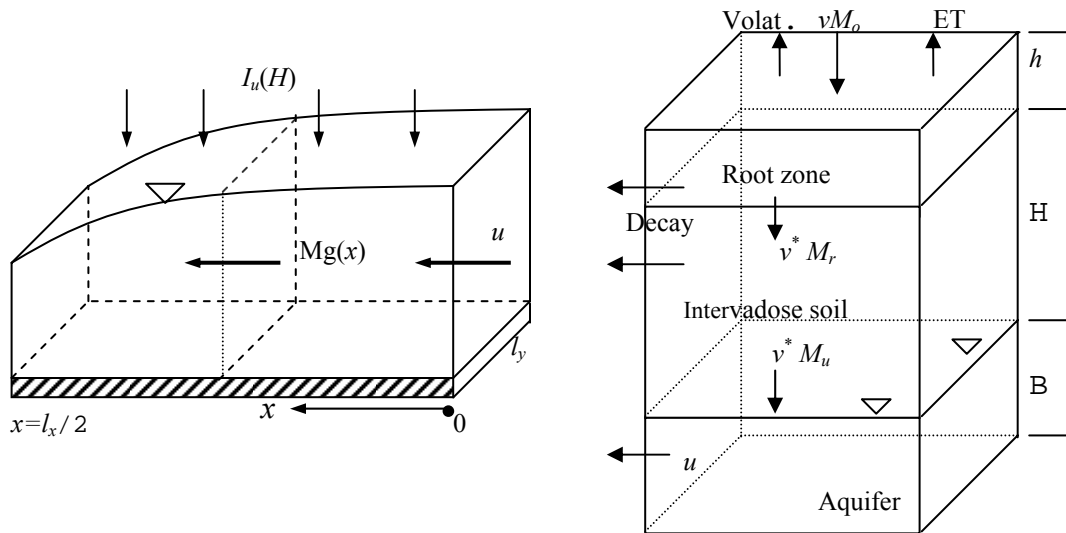

Fig.1. Conceptual soil-aquifer system

ET; $\mu = (F\,S+\sigma/h)\lambda/[0.693\,R_r\theta_r]$, R_r = liquid-phase partition coefficient, $R_r = 1+(\rho_b K_d+\kappa_r K_H)/\theta_r$; $\sigma = \kappa_r K_H D_g/d$; θ_r = average volumetric water content in the root zone; h = depth of the root zone [m]; ρ_b = bulk soil density [Kg/m^3]; λ = pesticide half-life [day^{-1}]; K_d = distribution coefficient [m^3/Kg]; κ_r = volumetric air content in the root soil; K_H = dimensionless Henry constant; S = transpiration rate [day^{-1}]; F = transpiration- stream concentration factor; D_g = gaseous diffusion coefficient [m^2/day]; and d = thickness of air boundary layer on soil surface. Equation (2) is based on the following assumptions: i) well-mixed root zone; ii) volatilization from soil surface occurs through an air boundary layer of thickness d; iii) first-order rate reaction; and iv) passive plant uptake – rate of uptake is proportional to dissolved solute concentrations.

One-dimensional transport and fate of solutes in the intermediate-vadose zone may be described by the following boundary value problem

$$\theta_u R_u \frac{\partial C_u}{\partial t} = -\frac{\partial F_u}{\partial z} - \theta_u R_u k_u C_u \tag{2}$$

Boundary conditions:

B.C. 1
$$F_u(0,t) = v^* C_r \tag{3}$$

B.C. 2
$$C_u(\infty,t) = 0 \tag{4}$$

Initial condition:
$$C_u(z,0) = 0 \tag{5}$$

where F_u is the solute flux, $F_u = -\theta_u D_u \dfrac{\partial C_u}{\partial z} + v^* C_u$; $D_u = (\kappa_u/\theta_u)K_H D_g + D_z$ is the effective

liquid-phase diffusion coefficient [m^2/day]; D_z = vertical dispersion in the soil [m^2/day]; θ_u = volumetric water content in the intermediate-vadose zone; $R_u = 1+(\rho_b K_d+\kappa_u K_H)/\theta_u$; $k_u = 0.693/\lambda$ is the decay rate coefficient [day^{-1}]; and κ_u = volumetric air content in the intermediate-vadose soil.

Leaching per unit area of soil, I(z,t), at depth z below the root zone at time t is defined by:

$$I_u(z,t) = \int_0^t F_u(z,\tau)\,d\tau \tag{6}$$

The application of the Laplace transformation to Eqs. (1) and (2), and the use of Eqs. (3)-(5) yield

$$\tilde{F}_u(z;p) = \tilde{F}_u(0;p)\ e^{-\frac{1}{2}\left[\sqrt{1+4\,T_u\ P_u^{-1}(p+k_u)}\,-1\right]\,P_u\frac{z}{H}}\,, \quad and$$

$$\tilde{F}_u(0;p) = M_o\,\frac{v^*/\theta_r}{h\,R_r}\,\frac{1}{\beta_r + p} \tag{7}$$

where $\tilde{f}(z;p) = \int_0^\infty f(z;t)\,e^{-p\,t}dt$, is the Laplace transform of the function $f(z,t)$, $T_u = H\,R_u/(v^*/\theta_u)$ is the residence time in the intermediate-vadose zone, and $P_u = H(v^*/\theta_u)/D_u$ is a Peclet number in the intermediate-vadose soil. The Laplace transformation of the leached-fraction function $I_u(z,t)$ follows immediately by applying the transform to (6): $\tilde{I}_u(z;p) = (1/p)\tilde{F}_u(z;p)$. Thus, residual solute mass that eventually leachs below depth z

is given by $I_u(z) = \lim_{p \to 0} p\, \tilde{I}_u(z;p) = \lim_{p \to 0} \tilde{F}_u(z;p)$, in which the substitution for $\tilde{F}_u(z;p)$ from (7) and taking the limit yields

$$I_u(z) = \frac{M_o}{1 + \ln(2)(T_r/\lambda)(1+\mu)} e^{-\frac{1}{2}\left[\sqrt{1 + 4k_u T_u P_u^{-1}} - 1\right] P_u \frac{z}{H}} \tag{8}$$

The first of the products on the right-hand side, I_r, accounts for the leached mass fraction below the root zone. This equation describes the interactions among the physical and biochemical processes and their net effect on vertical leaching in agricultural soils. Total emissions of the pesticide to the water table, I_u, can be obtained by the substitution of H for z in Eq. (8). Note that λ accounts only for biodegradation only, the effective half-life $t_{1/2}$, which also accounts for the effect of roots uptake and volatilization from the soil surface, is, thus, given by $t_{1/2} = \lambda/(1+\mu)$.

The evaluation of Eq. (8) requires average values for each of θ_r and θ_u. While θ_r may be assumed to attain the value at field capacity (e.g., *Rao et al.*, 1985), average θ_u can be estimated assuming quasi-steady gravity flow: $v^* = K(\theta_u)$ and using appropriate hydraulic conductivity-matric potential function (e.g., *Clapp and Hornberger*, 1978). An estimate for expected groundwater concentration may be given by $I_u/(n\,B)$; in which n = aquifer porosity, and B = thickness of the contaminant plume [m]. More details are given later in the application section for estimates of groundwater concentrations on the basis of multiple applications.

Emissions to ground water

Pesticides may undergo further attenuation along groundwater pathways because of dispersion and biochemical decay in the aquifer porous matrix. The residual solute mass convected across a plain normal to groundwater flow and below an agricultural plot of dimensions $l_x \times l_y$ (Fig.1) can be obtained by the integration of *Hantush and Mariño* (1997) solution, which describes two-dimensional and depth-averaged concentrations in ground water due to a rectangular nonpoint source, over the source area and in time:

$$M_g(x)/(M_u l_x l_y) = \frac{1}{P^* \sqrt{\gamma}} \left\{ \frac{\sqrt{\gamma}+1}{\sqrt{\gamma}-1} \left[1 - e^{\left(-\frac{\sqrt{\gamma}-1}{2} P^*(x/l_x + 1/2)\right)} \right] + \right.$$

$$\left. \left[1 - e^{\left(\frac{\sqrt{\gamma}+1}{2} P^*(x/l_x - 1/2)\right)} \right] \right\}, \quad x \leq l_x/2 \tag{9}$$

where $\gamma = 1 + 4\, T_g\, k/P^*$, $\rho = [(\gamma^{1/2}-1)/4]\, P^*$; $P^* = u\, l_x/D_x$ is a Peclet number; $T_g = l_x R_g/u$ is ground-water residence time [T]; and u is the average pore-water ground-water velocity [L/T]. Eq. (9) describes the integrated effects of dispersion and biochemical reactions on the residual mass flux of the contaminant past an aquifer section below and at a distance x downgradient from the center of the agricultural plot. It can be used to estimate residual mass of the pesticides entering a surface-water body (e.g., stream) downgradient from the

plot.

Implication on Management of Pesticides

A strategy for the management of organic compounds can be implemented by imposing an upper limit F^* on the leached fraction in order to screen out those pesticides that have the highest potential for ground-water contamination: $I_r \leq F^* M_o$, and I_r is the integrated mass flux (leaching) below the root zone. The substitution of the first of the products on the right-hand-side of Eq. (8) - recall, represents leaching below the root layer – for I_r in the above inequality and solving for T_r/λ yields

$$\frac{T_r}{\lambda} \geq 1.44 \left(\frac{1 - F^*}{F^*} \right) \frac{1}{1 + \mu} \tag{10}$$

To illustrate the aggregated effect of volatilization and uptake by natural vegetative cover, we consider the case $\mu = 1$ (typical to the pesticide bromacil, which has characteristics suitable for greater uptake by plants) and $\mu = 10$ (typical to the highly volatile heptachlor). Then for a leaching factor $F^* = 0.1$, the substitution for μ in (10) yields $T_r^* \geq 6.5 \lambda$ and $T_r^* \geq 1.2 \lambda$, respectively. Volatilization has much greater impact than crop uptake on the management process by extending the pool of environmentally acceptable pesticide; i.e., by expanding the list of relatively long-lived pesticides that can be used. Thus, the use of process driven screening models may have implication on cost-effective management of pesticides.

Nonpoint Source Assessment (*GIS*)

The study site (Locust Grove) is paired-watersheds of the Chester River drainage basin. The Chester River constitutes the southern boundary of Kent County, Maryland, and lies within the mid-Atlantic Coastal Plain along the northeastern shore of the Chesapeake Bay (Fig. 2). The land in the Locust Grove site is predominantly agriculture, used to grow mainly corn and soybeans in an annual rotation with winter wheat. Loamy soils, which range from sandy loam to clay loam, dominate the landscape in that area, and the surficial aquifer at the site consists of sand and gravel of fluvial origin. The relatively shallow water table and high conductivity of the aquifer favor greater vulnerability of ground water and stream baseflow to agricultural chemicals. The soil data is digitized from Kent County Soil Survey maps and complemented by soil hydraulic properties, including organic carbon fractions from available literature (e.g., *Carsel et al.*, 1988). Figure 3a classifies the soil in the study area according to hydrological groups. Figures 3b and 3c are ArcView GIS display of estimates of concentrations of the pesticide dicamba (commonly used for Wheat-barley-alfalfa and Soybeans) in the intermediate vadose zone, $I_r/(\theta_u H)$, and ground water, $I_u/(n B)$, respectively. The estimates are based on one application of 2.5 lb/acre and (February-April) climatic and hydrologic conditions.
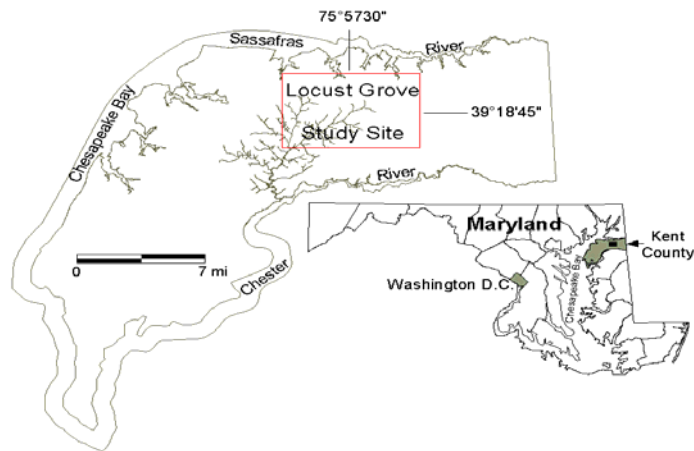
Fig. 2 Map of the study area (Locust Grove, Kent County, MD)

The above equations for the estimation of soil and groundwater concentrations are programmed, using avenue scripts, and the results shown in Figs 3a and 3b are based on running the scripts within the ArcView GIS project. Figure 4a displays the nonpoint source module (NPS_Modeling) built into the ArcView project menu. Some of the required input parameters are independent of soil features (or polygons in ArcView GIS), such as the temperature, precipitation, Henry constant, initial mass application, …etc., and they are entered for processing by the avenue scripts through a Visual-Basic-type user-interface features as shown in Fig. 4b.

The soils in Chesterville Branch appear to be primarily class B, whereas they are primarily class C in Morgan Creek (Fig. 3a). Thus, the former basin is relatively more drained than the latter, thereby resulting in greater expected maximum concentrations of dicamba in the intermediate-vadose zone and in ground water in the Chesterville Branch. The effect of the spatial variability of soil texture and drainage properties, and the depths to water table, is evident on the distribution of estimated concentrations in the intermediate-vadose zone and in ground water. The excessively estimated concentrations in the intermediate-vadose zone, especially toward the Sassafras River and in other isolated areas, are attributed to reference surface elevations where the depths to the water table approach zero, $H = 0$ m (Fig. 3b). Errors in kriged depths to the water table may also be a contributing factor. We emphasize that the estimated concentrations in the soil and ground water only present expected magnitudes and are short lived, especially those estimated in the soil (Fig. 3b), since they are associated with a single application of the pesticide. However, the estimated concentrations in ground water may persist for a longer period, especially for multiple applications of dicamba. If a pesticide is applied at a certain frequency, ω (in this application $\omega = 1$), a quasi-steady state may develop and the concentration in ground water can be estimated from
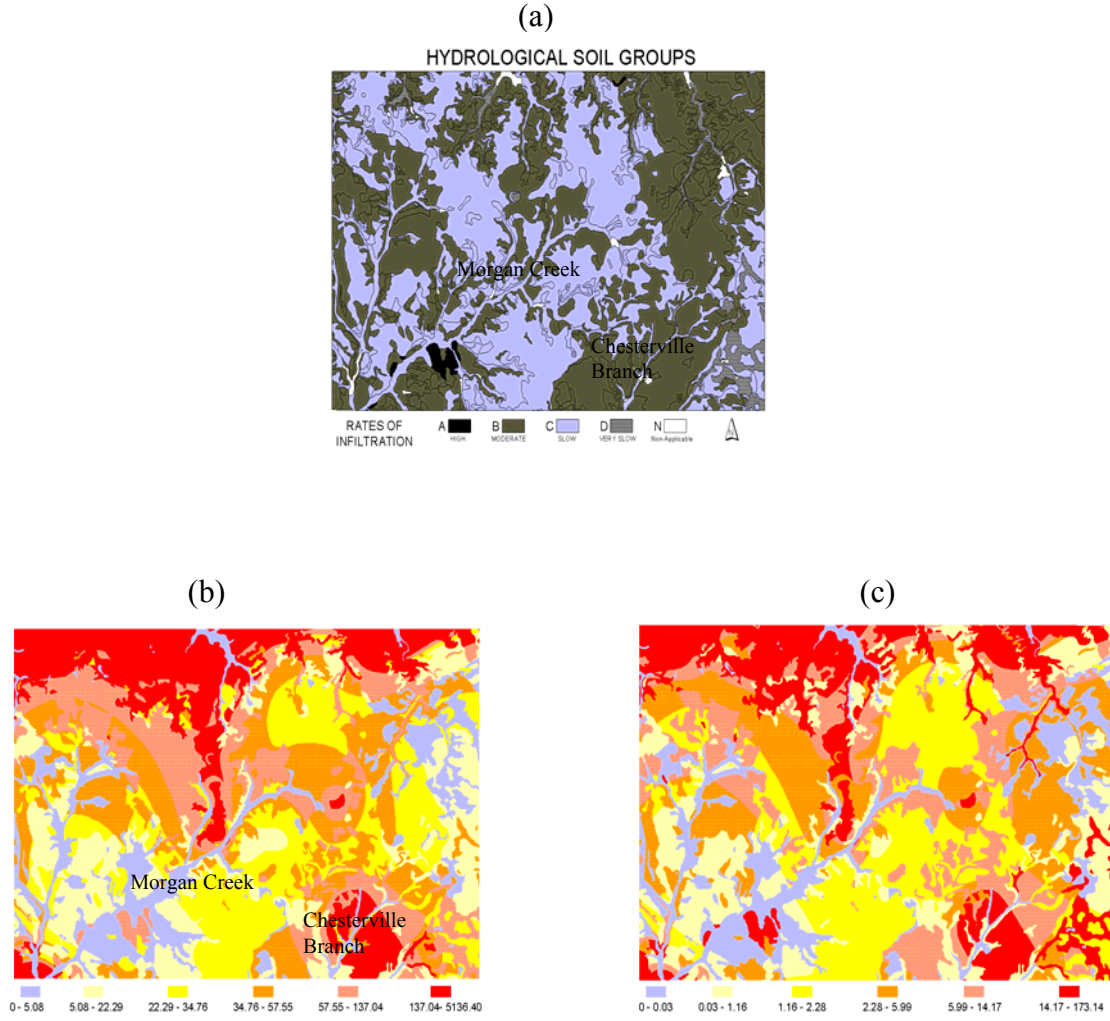
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Fig. 3 (a) Soil hydrological classes; (b) Estimated concentrations (ppb) of dicamba in the intermediate-vadose zone in Spring; (c) Estimated concentrations (ppb) of dicamba in ground water in Spring (the intermediate-vadose zone in Spring

$$C^{*}(j) = \frac{\omega I_u(j)}{n\,B} \tag{11}$$

in which $C^{*}(j)$ is an estimate of quasi-steady concentration in ground water (Kg/m^3) and j is an index, which accounts for seasonally-averaged hydrologic and climatic conditions. An alternative approach for calculating the quasi-steady state groundwater concentrations is to assume that applications of a pesticide are flushed into the water table during a given season by the cumulative recharge (in volume) (*Beltman et al.*, 1995):

$$C^{*}(j) = \frac{\omega I_u(j)}{P(j)} \tag{12}$$

Hantush

in which P(j) = is the cumulative recharge during season j [m^3].

As Fig. 3c shows, biodegradation of dicamba in the intermediate vadose zone (assuming half-life = 50 days) and mixing in the aquifer (B = 5m) have the potential of significantly reducing (by orders of magnitude) dicamba concentrations in ground water.

It is often the case that half-live values (λ) of pesticides that are reported in the literature lack sufficient details regarding the conditions under which they are measured, therefore, are subject to uncertainty. Information as to whether measured values of the half-lives were made in the laboratory or under filed conditions, is rarely sited in the literature. Field-measured half-life usually incorporate the combined effect of all possible loss pathways (biodegradation, volatilization, and crop uptake), and their use in physically based resolute models is bound to overestimate actual losses, and consequently, underestimate the magnitude of potential pollution problems. In case of uncertainty in reported values of λ, the effective half-life $t_{1/2} = \lambda/(1+\mu)$ can be treated as a random variable. And losses due biodegradation, volatilization, and crop uptake, are lumped into one parameter, $t_{1/2}$, rather than being evaluated individually (recall, data requirements for the estimation of S, σ, and μ).

Summary and Conclusions

A methodology is presented for the assessment of groundwater vulnerability to pesticides in agricultural watersheds. The methodology integrates simple but physically based analytical models with ArcView GIS to assess the fate of pesticides in the subsurface. The models describe the combined effect of the physical, (bio)chemical processes, and related environmental factors on the fate and transport of the organic solutes in the soil and ground water. The models are capable of describing leached mass fractions of solutes below the root zone, and the residual mass emissions to ground water. The leached mass fraction and residual mass emissions are estimated on the basis of cumulative mass flux past a particular section normal to the flow in the subsurface porous media. The resolution of the models is such that processes of crop uptake and volatilization of the pesticides can also be accounted for as well as advection, dispersion, equilibrium adsorption, and biodegradation. It is demonstrated that the ability to quantify potential loss pathways by crop uptake and volatilization may leads to improved (more cost effective) management of the pesticides, with the objective of protecting groundwater quality.

The modeling-GIS framework is applied to mid-Atlantic coastal plain agricultural watersheds for the assessment of potential impact of the use of the pesticide dicamba on groundwater quality. The primary objective of using ArcView GIS is to investigate the impact of the spatial variability of soil hydraulic, biochemical properties and other environmental factors on the variability of dicamba emissions to ground water. Preliminary estimates indicated that ground waters in the relatively well-drained areas around Chesterville Branch received higher doses of dicamba, probably due to relatively shorter residence time in the soil where (bio)chemical degradation has more impact than in the relatively poorly-drained areas in the Morgan Creek watershed. Further assessment is needed because of uncertainty in soil and hydrologic parameters and estimation errors in kriged depths to the water table. The input parameters were based on measured values and

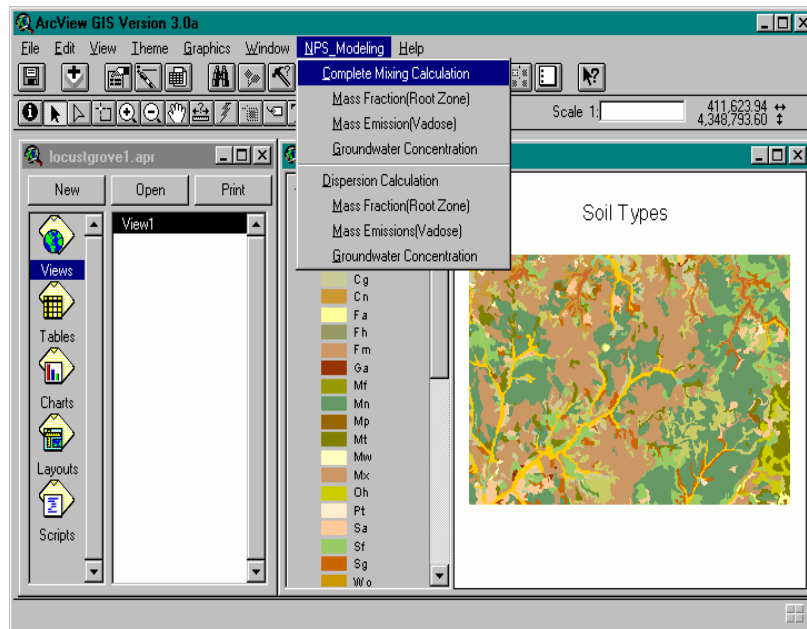average values reported in the literature.

Estimation of the impact of uncertainty of input parameters on the variance of the estimates of concentrations is currently under investigation, using first-order and second-order analysis.

Notice: This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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(a)

(b)

Fig. 4. Graphical user-interface features for the Nonpoint Source Assessment Module in ArcView GIS

Stratified Soil Profile

The semi-infinite solution of (8) is based on the assumption that dispersive flux is negligible when compared to advection. Shallow impeading layers (e.g., silty-clay layer or loess) can slow down convected solute fronts and produce a significant upward diffusive flux. A semiinfinite solution of Eq. (2) is not valid in this case.

The first equation in (7) is a general Laplace-transform representation of leaching in a distinct soil layer in a stratified soil. Starting with the upper most layer and assuming that a semiinfinte solution is valid, one can deduce that leaching below a stratified soil profile made of N layers is given by

$$\ln\left(\frac{I_N}{M_o}\right) = -\frac{1}{2}\sum_{i=1}^{N}\left[\sqrt{1 + 4\ln(2)\frac{T_u^{\,i}}{\lambda}(1+\mu_i)\,P_u^{\,i\,-1}} - 1\right]P_u^{\,i} \tag{9}$$

in which, $T_u^{\,i}$ and $P_u^{\,i}$ are the apparent residence time and the Peclet number of layer i, respectively, and $\mu_i = 0$ in layers where losses by root uptake and volatilization are negligible. This equation may be used to described leached residual mass fractions of pesticides in stratified soils. It accounts for the heterogeneity of the soil profile and spatial variability of its hydraulic and (bio)chemical properties. An estimate for expected groundwater concentration may be given by $I_N/(n\,B)$; in which n = aquifer porosity, and B = thickness of the contaminant plume [m].